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Evaluation of Liming Materials Derived From a Calcareous Beach Deposit in Hawaii

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CONTENTS

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R. E. GREEN[1]

INTRODUCTION

Acid soils are widespread in the high-rainfall areas of Hawaii. The application of high rates of acid-forming nitrogen fertilizers, associated with intense cropping, has resulted in pH values as low as 3.5 on poorly buffered soils. Strongly acid conditions generally intensify deficiencies of calcium and phosphorus and are frequently accompanied by excesses of soluble aluminum and manganese, which are toxic to some plants. Large quantities of good-quality liming material will be required in future years to reduce soil acidity and to sustain high production on the acid soils of Hawaii.

The calcitic and dolomitic limestones commonly used on the mainland of the United States are not found in Hawaii. However, coral reefs and shoreline deposits of calcareous sand provide large reserves of potential liming material. Pulverized coral rock and calcareous beach and dune sands are currently used as agricultural lime, as is the coarse "reject lime" removed by screening in the production of commercial hydrated lime. These materials vary widely in purity, fineness, and rate of reaction. Coral sand[2] is a carbonate material having a relatively large particle size and a slow reaction rate. Dune sand generally has a smaller particle size than beach sand but is contaminated with varying amounts of soil and organic matter which reduce the overall neutralizing value. Reject lime has a high neutralizing value, due to a high content of calcium hydroxide, and is relatively soluble in water. Such variability in liming materials may limit the usefulness of liming recommendations from a soil-testing laboratory, unless the pertinent characteristics of both the liming material and the soil are taken into account.

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[2]The term "coral sand" is used here in the nontechnical sense and refers to calcareous beach deposits, to which the coral organisms actually contribute only a small part (see REVIEW OF LITERATURE).

Liming recommendations in Hawaii, currently, are based upon the determination of lime requirement by a comparison of measured soil pH values with the appropriate neutralization curves, such as those published in Hawaii Agricultural Extension Service Extension Bulletin 54 (Foster and Matsusaka, 1952). Such a procedure may provide a satisfactory estimate of the amount of finely divided, pure calcium carbonate or its equivalent needed to change soil pH to a specified level, but evaluation of the liming material is left to the farmer or to the agricultural extension agent assisting the farmer. The objective of the present evaluation of Hawaiian liming materials is to provide information which will allow greater accuracy in estimating the rate of lime to apply to achieve a desired soil pH level. Special emphasis is given to the evaluation of particle size effects since both coral sand and reject lime are relatively coarse materials.

REVIEW OF LITERATURE

Considerable research has been done on the effectiveness of various agricultural limes, especially in the eastern half of the United States and in Europe, where acid soils must be limed for optimum growth of many crops. There are few published data dealing specifically with liming materials available in Hawaii. In the August 1964 issue of *Hawaii Farm Science,* which was devoted to the subject of liming, Younge and Plucknett (1964*b*) discussed some characteristics of Hawaii liming materials and emphasized the desirability of small particle size.

Factors to be considered in evaluating a liming material are: (1) the chemical nature of the active ingredient, (2) the purity, and (3) the fineness.

The chemical nature of the neutralizing ingredient or ingredients affects the neutralizing value and solubility of the material and determines which cations will be exchanged for hydrogen or aluminum on the soil exchange complex. The chemical composition of a calcareous beach deposit in Hawaii depends upon the relative amounts of skeletal material from various marine organisms. The principal organisms contributing to Hawaii's calcareous shore deposits, in the order of decreasing importance, are as follows: foraminifera, mollusks, red algae, echinoids, coral, and green algae (Moberly and Chamberlain, 1964). Carbonates in skeletal material differ in mineralogical form and Ca/Mg ratio. Corals and the green alga *Halimeda* contain aragonite[3]; foraminifera, red algae, and echinoids contain calcite; but mollusks may contain both. Consequently, the calcareous beach sands of Hawaii are predominantly calcitic. Chave (1954) found that the mineralogic form of the carbonate is the most important factor controlling

[3]Pure calcite and aragonite are both composed of calcium carbonate, but differ in crystalline form. Aragonite has orthorhombic crystals with less distinct cleavage and greater density than calcite, which has hexagonal crystallization.

the amount of magnesium in the skeletal material. The aragonite forms seldom contain over 1 percent magnesium carbonate, while calcitic remains often have 20 or 30 percent.

The conversion of beach sand to hydrated lime in a kiln might be expected to increase the water-solubility of the material considerably. At 25°C the water-solubilities of both aragonite and calcite are about 0.0015 g per 100 ml, which is much less than the solubility of calcium hydroxide—0.185 g per 100 ml at 0°C or 0.077 g at 100°C (Hodgman, 1960).

The purity of a material refers to the content of the active ingredients. As the purity decreases, the value of the liming material decreases. In general, liming materials which contain less than 80 percent $CaCO_3$ equivalent are considered low-grade lime. Handling costs are generally too high to allow the use of materials containing large amounts of impurities. Moberly and Chamberlain (1964) analyzed sand from 102 Hawaii beaches to determine what percentage of each sand sample was insoluble in dilute hydrochloric acid. The content of noncalcareous material ranged from 0 to 99 percent on different beaches, but only 16 of the 102 beaches had more than 50 percent acid-insoluble particles.

Fineness of materials affects both the spatial distribution of the particles in the soil and the rate of particle dissolution. DeTurk (1939) emphasized that uniformity of lime particle distribution and the number of particles per unit volume of soil were more important than actual water-solubility. When the limestone particle reacts with the soil the particle is quickly surrounded by a mass of more or less neutralized soil, which, according to DeTurk, has a diameter of 0.25 to 0.5 inch. When the neutralized soil spheres overlap each other, the soil is completely neutralized. Obviously, a given small weight of large lime particles widely spaced in a large soil volume would not be as effective in neutralizing the soil as the same weight of very small particles. White (1917) studied the solubility of calcitic limestone in carbonated water and in soils to determine the relative activity of the various particle sizes. The activity of particles was found to be inversely related to particle diameter. Particles with mean diameters of 0.215 mm, 0.59 mm, and 1.9 mm were, respectively, 57, 27, and 18 percent as effective as 0.125-mm particles in correcting soil acidity. The calculated relative surface areas for the same sizes are 58, 21, and 7 percent, respectively, indicating good agreement between calculated relative surface and measured effectiveness.

Attempts have been made to quantify estimates of the particle size effect. Bear and Allen (1932) calculated the relative efficiency of different particle sizes on the basis of an equal reduction in particle diameter for all particle sizes in a given period of time. Thus the proportion R_i of the material in the ith size class which remains after the mean diameter d_i has been reduced by an amount a would be $R_i = [(d_i - a)/d_i]^3$. Schollen-

berger and Salter (1943) obtained experimental values of *a* for calcite of 0.056 mm, 0.117 mm, and 0.175 mm for reaction periods of 3 months, 1 year, and 4 years, respectively. Motto and Melsted (1960) used 0.064 mm for the value of *a* to calculate the expected relative efficiency of different particle sizes and found that experimental values agreed favorably with calculated values for two out of three soils. The validity of the equal-reduction hypothesis was tested experimentally by Elphick (1955) with several liming materials. His results, and a subsequent evaluation of his data by Swartzendruber and Barber (1965), showed that the rate of change of particle diameter was not constant for different particle sizes—with decreasing particle diameter the rate of reduction increased.

Evaluations of the relative effectiveness of various particle sizes by different investigators have yielded variable results, probably as a result of different experimental conditions. Soil properties affect reaction rates, as do temperature and soil moisture levels (Shaw, 1960). Although there may be merit in considering the relative efficiency of liming materials on the basis of specific surface or reduction in particle diameter with particle dissolution, the best evaluation of a given material appears to be an actual test of reaction rate under appropriate experimental conditions.

The importance of sufficient fineness of liming materials is reflected in the particle size requirements of most states in the United States. Lawton and Kurtz (1957) give the following information: "In the Agricultural Conservation Program, the specifications of 16 states for standard ground limestone require that 25 percent or more of the material must pass a 100-mesh sieve. Five states have set a requirement of 30 to 50 percent of the total to pass a 60-mesh sieve. Fineness of lime is emphasized in Northeastern States and Ohio and North Carolina, which gave assistance payments for lime in 1953 only when 40 percent of a limestone passed a 100-mesh sieve. Eleven states had no specifications regarding material finer than 10- or 20-mesh."

The sizes of sand particles on the beaches of Hawaii depend upon the nature of the reef and the wave action. The beaches having the finest grain sizes are generally on the windward coasts. Moberly and Chamberlain (1964) found that the median grain size for all the beaches on each of the islands varied from 0.30 mm (Maui) to 0.54 mm (Molokai).

PROCEDURES

Liming Materials Study

The liming materials used for this study, coral beach sand and reject lime, were both obtained from the Hawaiian Commercial and Sugar Company lime factory near Paia, Maui. The beach sand came from the stockpile used to supply the kiln in the manufacture of hydrated lime. The reject lime includes all particles greater than 0.074 mm in diameter that are

removed by sieving. Coral dune sand was not included in the particle size effect study due to the low neutralizing value (59% $CaCO_3$) indicated by one sample collected from the dune area of Maui. Reaction rates of equivalent particle sizes of dune sand, beach sand, and crushed coral should be comparable, so that data obtained for beach sand should apply to other coral liming materials.

The particle size distribution of liming materials was determined with sieves having the following openings in millimeters: 8.0, 4.0, 1.65, 1.0, 0.50, and 0.25.

Neutralizing value was determined by digestion of lime samples in 0.5 *N* hydrochloric acid and titration of the remaining acid with standard 0.25 *N* sodium hydroxide.

Carbonate content of liming materials and the residual lime in the soil neutralization study were determined by wet combustion and absorption of carbon dioxide as described by Allison (1960).

Calcium and magnesium were determined by titration with EDTA, the calcium being separated from magnesium by precipitation of calcium sulfate as described by Barrows and Simpson (1962).

The evaluation of reaction rate of liming materials was accomplished by two experiments in which liming materials were applied to a soil and allowed to react for different periods of time, after which the pH of a 1:1 soil:water mix was measured with a Photovolt Model 115 pH meter. The soil used was obtained from the no-lime plots of an old lime experiment on the Haleakala Experimental Farm near Makawao, Maui. Samples were taken from the 0- to 8-inch depth on three replicates and composited for the lime materials study. The soil is classified as Makawao silty clay loam, a Humic Latosol. The soil was air-dried and passed through a 2-mm sieve before lime additions.

The results obtained by White (1917) indicate that the calculated specific surface of liming materials might allow one to estimate the rate of a material needed to increase the pH to a specified level. Such a procedure might be especially useful to estimate short-term pH response for a given liming material, since farmers seldom allow much time for lime reaction between the time of lime incorporation and crop planting. In the first reaction rate study, unsegregated liming materials and particles in various size groups were applied on the basis of equivalent specific surface to determine if the short-term pH response of limed soil could be predicted from the particle size distribution of liming materials. The particle surface was calculated by assuming spherical particle shape and equal particle density for each particle size of a given material. Particles which passed a 0.25-mm sieve were arbitrarily assumed to have a mean particle diameter of 0.15 mm and were applied at a rate of 5 me base per 100 g soil. Particles in size groups with mean diameters greater than 0.15 mm were applied at

rates providing surface areas equivalent to that of the 0.15-mm group. The weight of particles in the ith size group with mean diameter d_i necessary to give the same surface area as 1.0 g of particles with a mean diameter of 0.15 mm is given by the ratio of the specific surfaces, $S_{0.15}/S_i$. Since the specific surface (area per unit weight) of a material is given by the relation $S_i = c/d_i$, where c is a constant which is determined by the density of the material,[4] the ratio $S_{0.15}/S_i$ can be reduced to $d_i/0.15$, or $6.67\ d_i$, which relation was used to calculate the weight to apply of each size group on an equivalent surface area basis. The amount of unsegregated liming material to apply on the equivalent surface area basis is given by the summation of quantities calculated for each size group as follows:

$$S = \sum_{i=1}^{6} (6.67\ d_i)(P_i)$$

where S = grams of unsegregated liming material with a calculated surface area equal to that of 100 g of 0.15-mm material

d_i = mean diameter in millimeters of particles in the ith size group

P_i = percent by weight of each size group in the unsegregated liming material, determined by particle size analysis.

(Note that $\sum_{i=1}^{6} P_i = 100\%$.)

The appropriate amount of each material, including a treatment of reagent grade calcium hydroxide, was applied to a quantity of air-dried soil equivalent to 50 g of oven-dried soil. Treatments were replicated to provide duplicate samples for each measurement period. The soil and liming material were well mixed, placed in a small glass bottle, and wet with distilled water to a moisture content corresponding to 0.2-bar soil-water suction. The sample bottles were randomized, covered with paper but not sealed, and stored at room temperature (about 70°F). Soil water lost by evaporation was replenished monthly. The pH of the 1:1 soil:water mixture was read at periods of 1, 3, and 6 months after application of all materials and also at 9 months for the unsegregated materials. Readings of pH were taken

[4]The constant c, in the relation $S_i = c/d_i$, cancels out in the ratio $S_{0.15}/S_i$ if the particle density is assumed constant for each particle size group. If the particle densities ρ_i are known and are different, the value of c would be given by $6/\rho_i$, where the specific surface is given by the relation $S_i = \pi d_i^2/[\rho_i(1/6\ \pi\ d_i^3)] = 6/\rho_i\ d_i$. The relationship between specific surface and particle diameter for spherical particles having the density of aragonite (2.9 g/cm^3) is shown in figure A-1 in the Appendix. A sharp increase in specific surface with decreasing particle diameter for diameters < 0.5 mm is apparent.

within 5 minutes of mixing the water and soil to reduce errors due to the further reaction of large particles of reject lime upon particle breakdown with stirring. However, even with this precaution, the greatest variation occurred on soil samples treated with large diameter particles of reject lime.

The second portion of the laboratory study was designed to determine more precisely the quantity of each particle size which would give a pH change equal to that of a given quantity of calcium hydroxide. All materials were compared at 10 and 30 me per 100 g, and the pH was measured after 3 months, a sufficient period to reach near-maximum pH for each treatment as indicated by the first laboratory trial.

Soil neutralization curves were determined with both calcium hydroxide and sodium hydroxide to compare the results obtained using these two bases in dilute suspensions (1:10 soil:water ratio) with the pH response from the application of solid liming materials to soil. The pH was measured after a 1-week equilibration period.

A field liming trial was conducted on the Makawao soil from which soil samples had been taken for the laboratory analysis. Unsegregated coral sand and reject lime were applied at rates calculated to give a specific surface equivalent to that of 5 me of 0.15-mm material per 100 g soil. The surface layer of the soil into which the lime was incorporated by rototiller was calculated to weigh approximately 2 million pounds per acre. Although the lime was applied on August 12, 1963, the soil remained relatively dry until 1.47 inches of rain fell September 16–18. The subsequent sampling periods were, therefore, determined from the latter date. A composite sample of 10 soil cores from the 0- to 6-inch depth on each plot was taken at 1, 6, and 9 months for pH and carbonate analyses. Except for one tillage, about 1.5 months after the initial tillage following lime application, the field remained untilled. *Desmodium intortum* was planted in the field after the final tillage.

In addition to field data obtained from the trial discussed above, pH response data from a liming experiment on the Kula loam soil[5] are presented to provide additional information on the accuracy of liming recommendations based on a knowledge of the properties of both the soil and liming material.

Residual Lime Effects Study

Soil samples were taken from old liming experiments at three locations to determine pH, residual carbonates, calcium, and magnesium. One experiment was located on a Humic Latosol soil (Makawao series), one on a Humic Ferruginous Latosol (Pauwela series), and one on the Uaoa series,

[5]The latosolic Reddish Prairie soils in the Kula area of Maui have been designated Kula loam in a recent tentative revision of the classification of Hawaiian soils. Previously this soil was identified as Waimea loam.

a colluvial soil associated with the Pauwela series. All three soils are quite acid and require liming for many crops. The experimental locations were used for pasture or forage experiments in the past and had grass-legume cover at, or shortly before, the time of sampling.

Soil samples were air-dried and ground to pass a 1-mm sieve for analysis. A 1:1 soil:water mixture was used for pH analysis. Exchangeable calcium and magnesium in the soil were determined on the ammonium acetate (1 *N*, pH 7) leachate. The ammonium adsorbed by the soil in the removal of exchangeable cations was then removed by leaching with normal KCl and distilled into boric acid for the cation exchange capacity determination.

RESULTS

Liming Materials

Physical and chemical characteristics of the coral beach sand and reject lime used in the laboratory experiment are shown in table 1.

Particles greater than 1.65 mm and less than 8 mm were included in the particle size analysis but data for these sizes are not shown in table 1. Particles in this range comprised 8.2 percent and 6.4 percent of the coral sand and reject lime materials, respectively. Particles greater than 8 mm in diameter were not included in the particle size analysis, but comprised only 0.1 percent or less of the total material. The particle size data show that the size distribution of coral sand and reject lime differed principally in the $\leq$ 0.25-mm and 0.75-mm fractions. About 90 percent of both materials passed a 10-mesh (1.65-mm) sieve while about 20 percent of the coral sand and 9 percent of the reject lime passed a 60-mesh (0.25-mm) sieve.

The bulk density of the various size groups of coral sand did not differ widely, while for reject lime the $\leq$ 0.25-mm fraction had a lower density than other fractions. The low density of the small diameter particles is probably due to both the greater porosity and higher hydroxide content of this size group.

A comparison of the neutralizing value and carbonate content of each material and size group shows that the coral sand is essentially all in the carbonate form and is relatively pure (96 to 97 percent $CaCO_3$). The carbonate content of reject lime is much lower than that of the coral, but the neutralizing value of reject lime is higher due to the presence of the hydroxides of calcium and magnesium. The higher percentage of carbonates in the larger reject particles suggests the failure of large calcium carbonate particles to convert to the oxide in the lime kiln. However, analysis of powder samples of the largest and smallest size groups of both materials by X-ray diffraction revealed the presence of both calcite and aragonite in the calcareous sand, while the reject lime was found to contain only calcite. Thus the calcium carbonate in reject lime was probably not residual skeletal material but recrystallized calcite formed by the reaction of calcium hydroxide with atmospheric carbon dioxide.

TABLE 1. Physical and chemical properties of two liming materials derived from a calcareous beach deposit

MATERIAL	MEAN PARTICLE DIAMETER	WEIGHT PERCENT OF WHOLE MATERIAL	BULK DENSITY	NEUTRALIZING VALUE	CARBONATES	CALCIUM	MAGNESIUM
	mm	*%*	*g/cm³*	*% of $CaCO_3$*	*% of $CaCO_3$*	*% of $CaCO_3$*	*% of $MgCO_3$*
Coral sand	Unsegregated	100.00	—	96.3	—	—	—
	≤0.25	19.84	1.33	95.4	96.1	90.1	2.9
	0.37	26.19	1.27	96.1	96.8	—	—
	0.75	25.31	1.27	96.8	96.4	88.8	7.6
	1.30	20.43	1.40	97.3	97.0	—	—
Reject lime	Unsegregated	100.00	—	105.6	—	—	—
	≤0.25	9.23	0.57	116.2	32.9	106.2	8.2
	0.37	27.15	0.88	106.2	56.9	—	—
	0.75	40.27	0.88	104.4	56.9	91.5	8.0
	1.30	16.95	0.88	102.5	55.6	—	—

Calcium and magnesium contents in table 1 are expressed as the carbonates. On a chemical equivalent basis the magnesium content is as high as 10 percent of the calcium content and thus would contribute to the magnesium status of soils to which the lime is applied.

Lime Applications on Equivalent Surface Area Basis

Based on the surface area of 1 unit weight of 0.15-mm material, the weight factors[6] for other particle sizes are 2.5, 5.0, and 8.7 for diameters of 0.37 mm, 0.75 mm, and 1.3 mm, respectively. Thus, 5.0 g of 0.75-mm material has approximately the same surface area as 1.0 g of 0.15-mm material. These weight factors were used to calculate application rates for each size group and for unsegregated materials, with the basic rate for the 0.15-mm material set at 5 me Ca per 100 g soil. Weight factors for unsegregated liming materials were 5.5 for reject lime and 5.4 for coral sand.

The change in pH with time in laboratory samples is shown for segregated particle sizes in figure 1. The soil pH prior to liming was 4.5. Reagent grade calcium hydroxide was applied at 5 me per 100 g of soil. Segregated particles were all applied at rates giving particle surface areas equivalent to the 5-me rate of the 0.15-mm size. The following observations are made from data in figure 1:

(1) Reject lime and coral sand particles passing a 60-mesh sieve (≤ 0.25 mm in diameter) reacted completely with the soil in 1 month or less.

(2) Reject lime particles > 0.25 mm, applied on the particle surface area basis, resulted in 1-month pH values far above the pH reached by 0.15-mm particles applied on a chemical equivalent basis.

(3) One-month pH values for coral sand indicate that the extent of lime particle reaction was approximately that predicted by particle surface calculations. Measurements at 3 and 6 months showed that coral particle dissolution after the 1-month period continued to increase the pH, as would be expected.

(4) A comparison of lime response for reject lime and coral sand at 1 month shows that reject lime reacts with the soil much faster than the less soluble coral sand. However, the coral continues to react, increasing the pH in a near-linear fashion after 1 month.

A comparison of the pH response of field soil and laboratory soil samples to applications of coral sand, reject lime, and hydrated lime is shown in figure 2. The data are expressed as the increase in pH over the check, since the pH of the field check plot varied considerably with time. At 9 months the pH increase for coral sand was the same for the laboratory and field

[6]The term "weight factor" is used to designate the weight of liming material of a given particle size which has a calculated surface area equivalent to a unit weight of particles having a mean diameter of 0.15 mm.

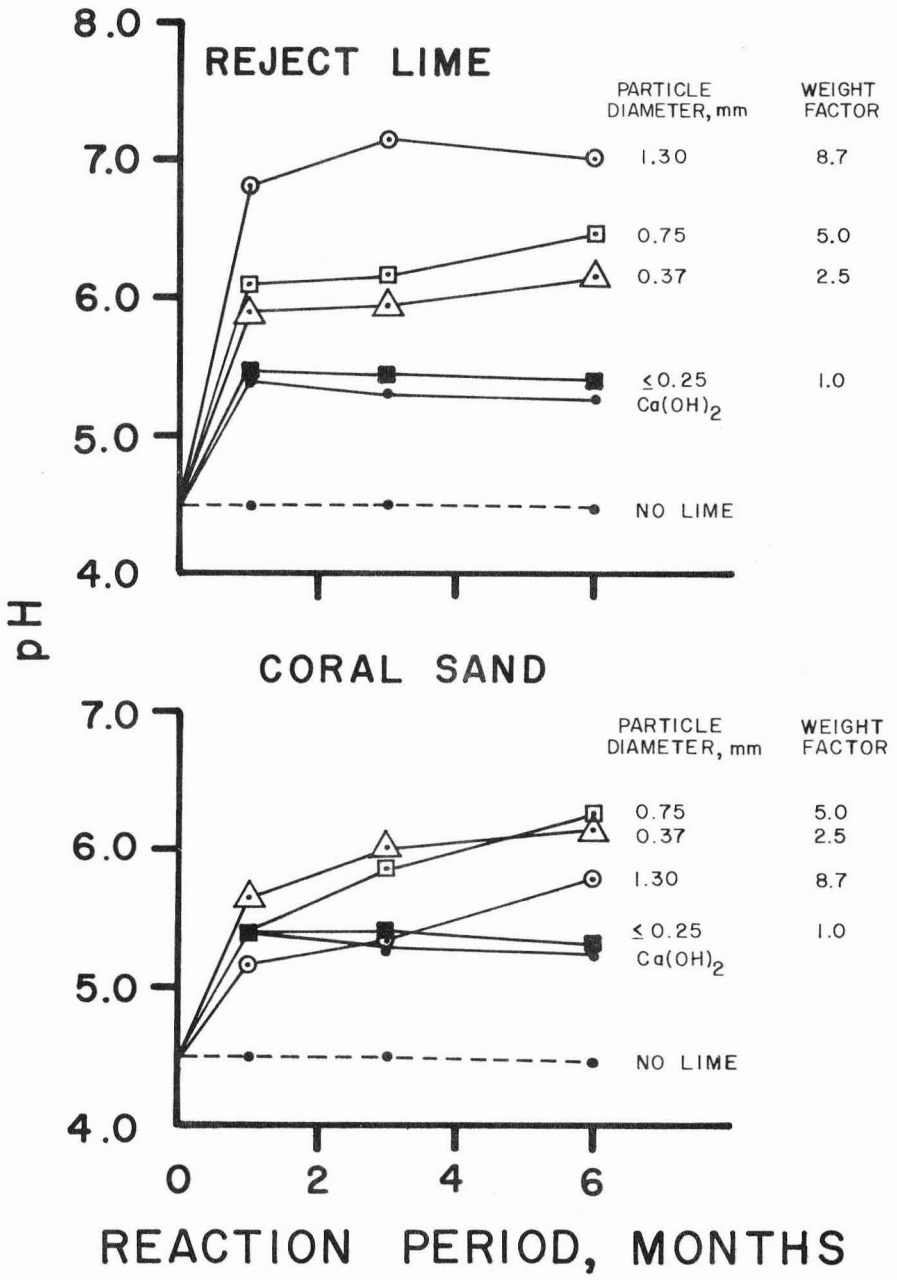

FIGURE 1. Change in pH of Makawao soil in the laboratory after application of reject lime and coral sand particles at rates based on the surface area of 5 me of 0.15-mm particles per 100 g soil.

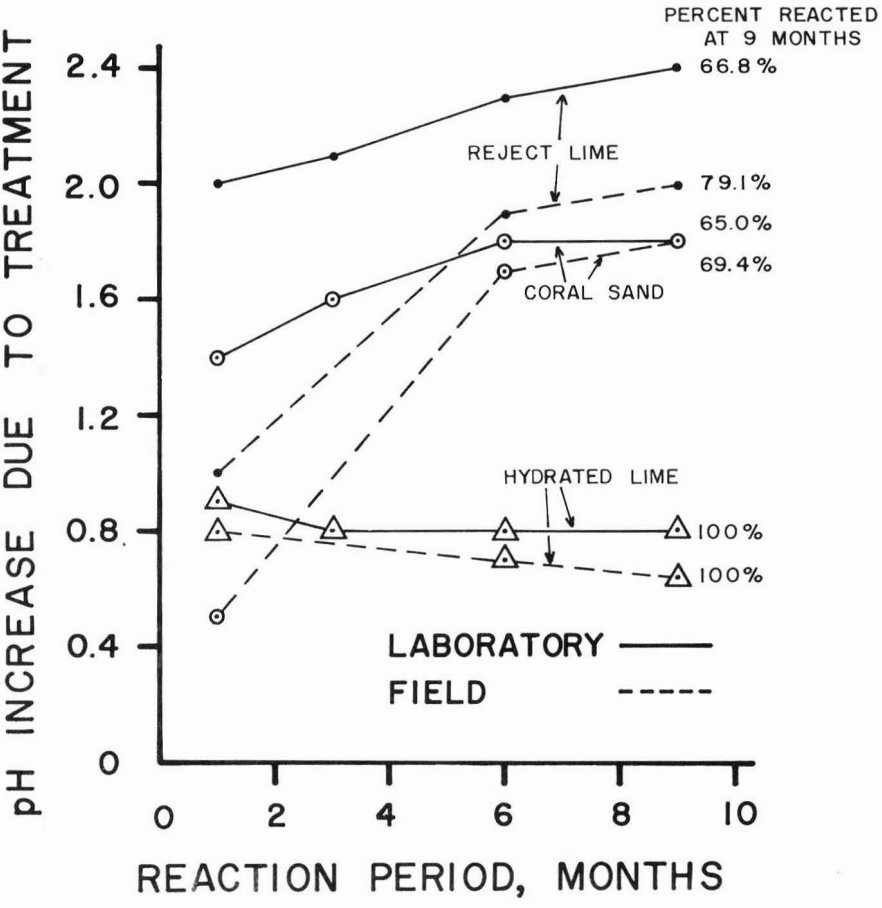

FIGURE 2. Soil pH response and percent of lime reacted in the laboratory and field after application of liming material to Makawao soil at rates calculated to give a surface area equivalent to 5 me of 0.15-mm material per 100 g soil. (Weight factors: coral sand, 5.4; reject lime, 5.5. pH of unlimed soil: laboratory, 4.5; field, 4.6 to 5.0.)

samples, while the pH increase from the reject lime application was 0.4 pH unit higher in the laboratory than in the field. This difference in pH response to reject lime may be due in part to a difference in particle size distribution, since the lime materials applied in the laboratory and field were not from the same batch. However, both batches of lime were from the same kiln and probably not greatly different. It is likely that periodic low soil moisture levels in the field limited the efficiency of field-applied reject lime more than coral sand, relative to the efficiency of these two materials in the laboratory. The calculation of application rate on the basis of equivalent

surface area was reasonably accurate for the field soil at the 1-month sampling. After 1 month the remaining lime continued to react, causing a further increase in pH. Analysis of field soil 21 months after application showed increases in pH due to liming to be 0.5, 2.2, and 2.2 for hydrated lime, reject lime, and coral sand, respectively.

Soil sampled at 9 months after lime application in both the laboratory and field was analyzed for residual carbonates. The percentage of lime which reacted with the soil is also shown in figure 2. The efficiency of applied lime was greater in the laboratory evaluation than in the field since the maximum pH increase in the laboratory was obtained with a smaller percentage of the applied lime reacting.

Lime Applications on Chemical Equivalent Basis

The soil pH responses in the laboratory 3 months after application of 10 and 30 me Ca in the form of $Ca(OH)_2$, coral sand, and reject lime are shown in figure 3. The curves demonstrate that the $\leq$0.25-mm material is equivalent to reagent grade $Ca(OH)_2$ when applied on the basis of chemical equivalence, while larger particles are less effective in a 3-month period, the degree of effectiveness being inversely proportional to the particle diameter.

The ratio [me $Ca(OH)_2$]/[me specified particle size] was calculated from data in figure 3 and is used to indicate the relative efficiency of various particle sizes in figure 4. The assumed efficiency ratio for short-term reaction used earlier (page 8) to calculate application rates based on particle surface area also is shown as a function of particle diameter in figure 4. The failure of the measured efficiency ratios to approach the calculated ratios demonstrates again that lime particles greater than 0.25 mm in diameter react much more than is predicted by surface area calculations. The curves in figure 4 show that (1) for particle diameters greater than 0.7 mm, reject lime is more efficient than coral sand, and (2) the decrease in efficiency with both increasing particle diameter and rate of application is greater for coral particles than for reject lime particles.

Data in figure 3 were also used to calculate the fraction R of material of each size remaining in the soil 3 months after application. The average reduction a in particle diameter d was then calculated according to the concept of Bear and Allen (1932), where $R = [(d-a)/d]^3$, or, rearranging terms, $a = d(1-\sqrt[3]{R})$. Values of a were found to vary from 0.08 mm to 0.16 mm for coral sand and from 0.15 mm to 0.27 mm for reject lime, with the value of a decreasing with increased particle diameter for coral sand, and increasing with particle diameter for reject lime. This difference between materials probably results from differences in solubility associated with the low water-solubility of coral particles, as the coral must react with acid soil to dissolve appreciably. The calcium hydroxide in reject lime, on

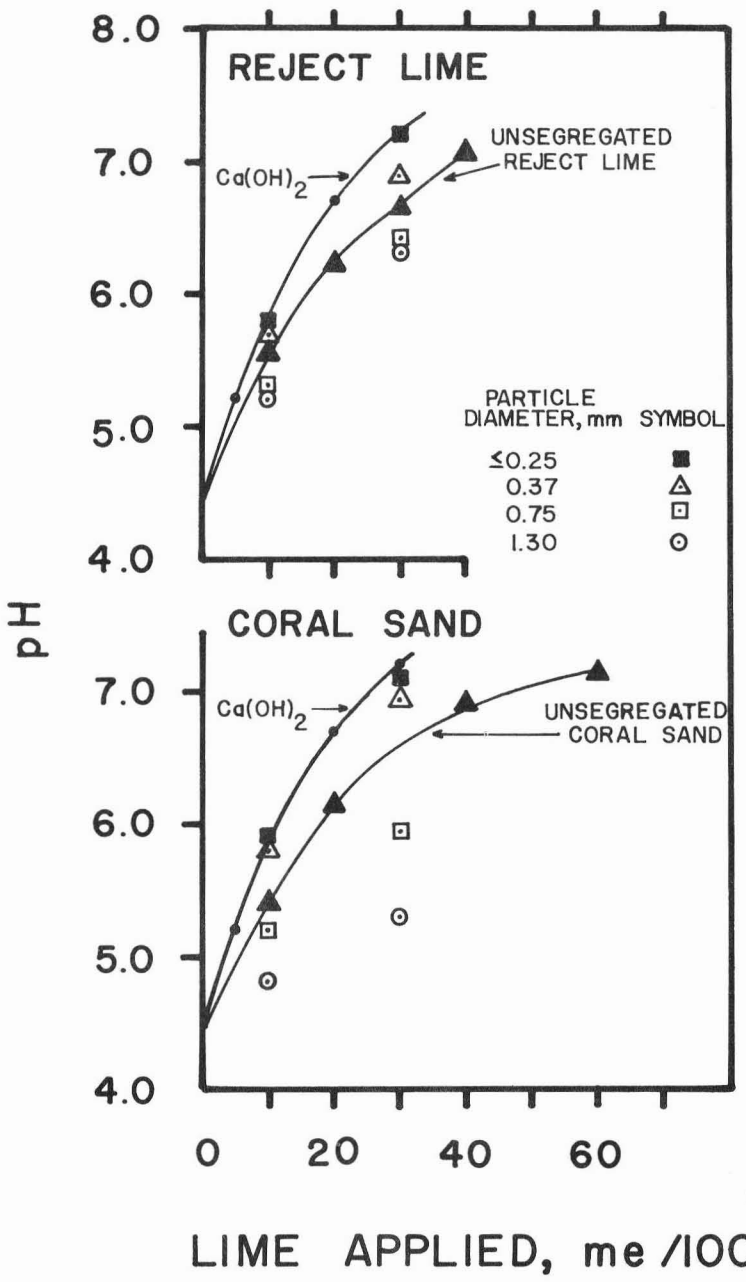

FIGURE 3. pH of Makawao soil in the laboratory 3 months after application of unsegregated and segregated particles of reject lime and coral sand.

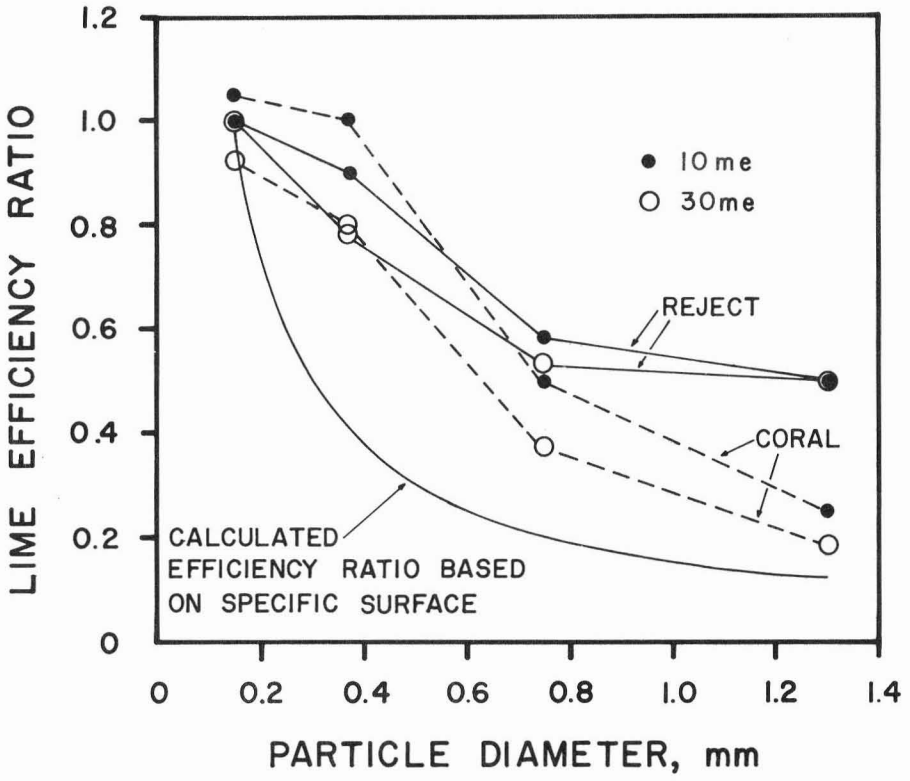

FIGURE 4. Relationship between lime particle size and 3-month efficiency ratio for reject lime and coral sand particles applied at two rates. Lime efficiency is expressed by the ratio [me $Ca(OH)_2$]/[me specified particle size], at the same pH, and was calculated from the data in figure 3.

the other hand, dissolves more readily even in neutral soil solution and would thus move by diffusion and neutralize a relatively large volume of soil. The value of *a* decreased with increasing application rate for both materials. Thus, the assumption of equal reduction in particle diameter for all sizes is invalid for these materials and of little value as a method of estimating particle size effects on the rate of lime reaction.

The effect of application rate on the efficiency of unsegregated lime is shown in figure 5. The greater solubility of $Ca(OH)_2$ in the reject lime probably explains the high efficiency of reject particles as compared to coral sand. The curves in figure 5 provide the information needed to calculate the amount of liming material, of known neutralizing value, to apply when

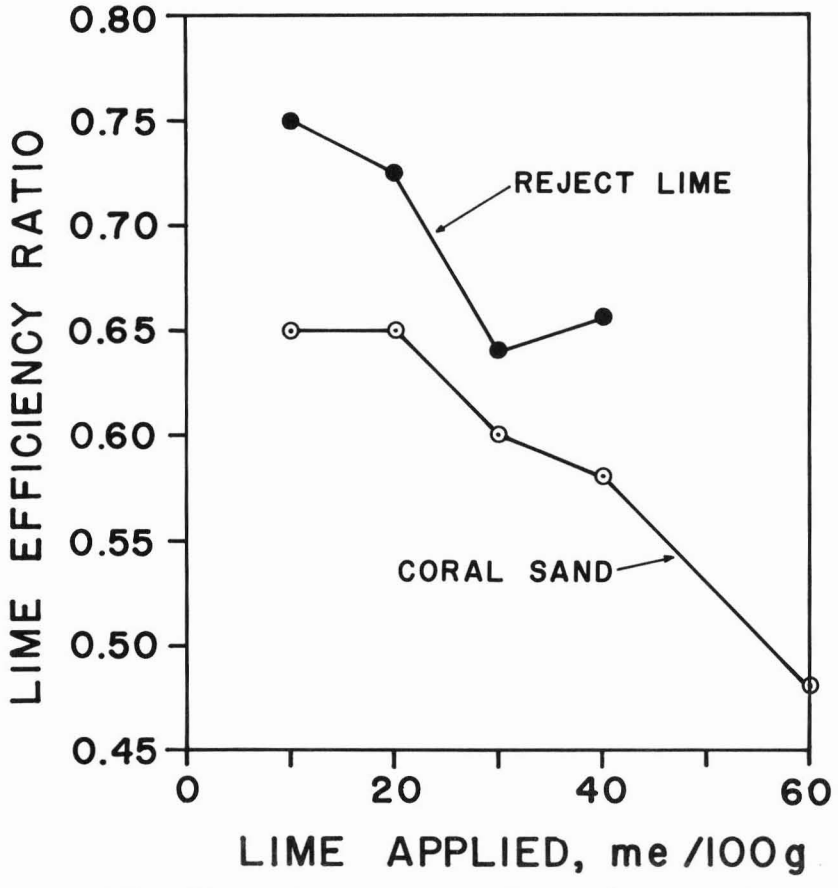

FIGURE 5. Effect of lime application rate on the efficiency of unsegregated reject lime and coral sand as measured in the laboratory after 3 months' reaction.

the soil pH and neutralization curve have been measured. The experimental "weight factors" (based on measured efficiency rather than on the efficiency predicted by particle surface calculations as defined in footnote 6) are given by the reciprocal of the measured efficiency ratios. At the 10-me rate the weight factors are 1.3 and 1.5, respectively, for reject lime and coral sand. Thus, at rates normally used in field practice, the reject lime evaluated in this study should be applied at about 1.3 times the rate of pure, finely divided $CaCO_3$, while the factor for coral sand is about 1.5. These weight factors (to account for the loss of efficiency due to large particle size) are lower than those obtained for the same materials by the summation of the

products of the weight factor for each particle size (calculated from figure 4) and percent by weight of each size group (table 1), which procedure yields values of 1.5 for reject lime and 2.1 for coral sand at the 10-me rate. The reason for the discrepancy between the measured and calculated weight factors is not apparent.

Field data from another lime study (Green, 1965) conducted on the Kula soil indicate a weight factor of 1.2 to 1.4 for reject lime applied at 15 me per 100 g. Since the Kula soil is highly buffered and the measured efficiency of reject lime on this soil is nearly the same as that obtained on the Makawao soil, the constancy of the efficiency ratio on soils of varying buffering capacity appears likely.

Chemical Properties of Soils

The pH response to applied lime of good quality depends largely upon the buffering capacity of the soil. Matsusaka and Sherman (1950) have shown that great differences exist in the buffering capacity of the several Hawaiian Great Soil Groups, due primarily to differences in mineralogy. Kanehiro and Chang (1956) have shown a distinct positive relationship between soil cation exchange capacity and buffering capacity.

The pH, cation exchange capacity, and exchangeable calcium and magnesium levels of the soils on which the residual effects of liming were studied are shown in table 2. All three soils have relatively low exchange capacities, and the low calcium and magnesium levels indicate extremely low base saturations.

TABLE 2. Properties of three latosolic soils. Soil samples were taken from the unlimed plots of liming experiments described in table 3

SOIL	pH	CEC	Ca	Mg
		me/100 g	*me/100 g*	*me/100 g*
Makawao silty clay loam	4.6	20	2.5	0.5
Pauwela silty clay	4.9	16	0.5	0.4
Uaoa silty clay loam	4.8	18	0.8	0.7

Neutralization curves for the same soils are shown in figure 6. A comparison of sodium and calcium neutralization curves for the three soils reveals that the ratio of me $Ca(OH)_2$ to me NaOH necessary to give the same pH varies from 2.3 to 2.9 on the Makawao soil and from 1.9 to 2.9 on the Pauwela and Uaoa soils, the highest ratio occurring at the 5-me rate of

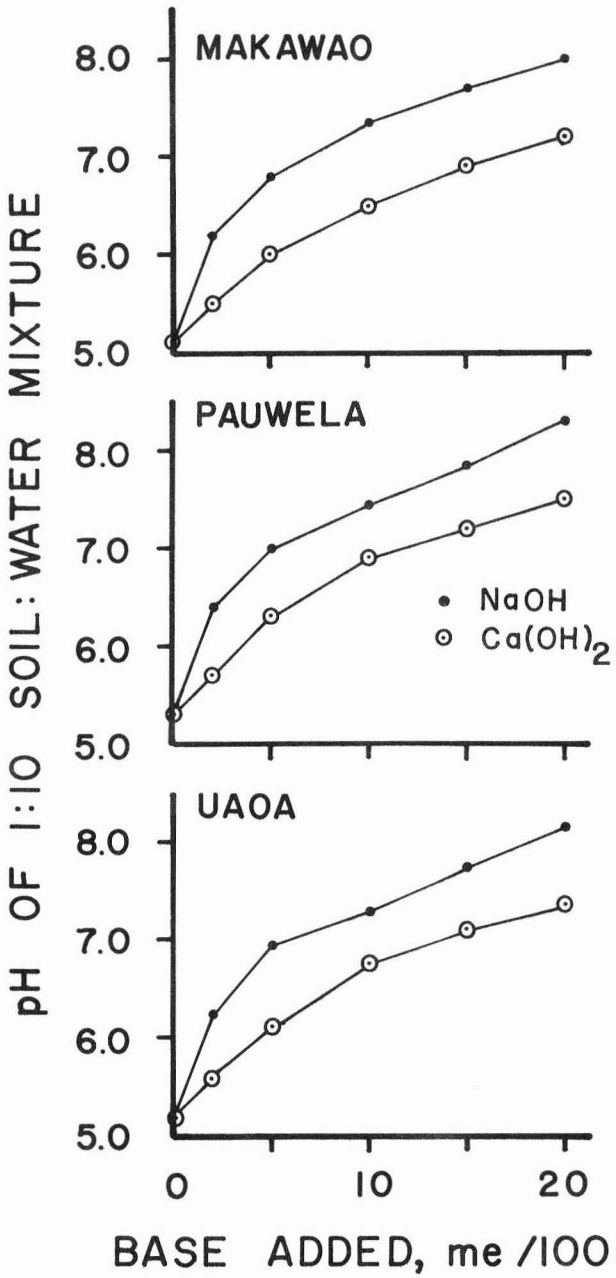

FIGURE 6. Neutralization of three latosolic soils with sodium and calcium hydroxides. pH was measured 1 week after base addition to the soil.

TABLE 3. Lime treatments of old experiments and the resulting residual pH and calcium on three latosolic soils

SOIL	LOCATION	ELAPSED TIME SINCE APPLICATION	LIMING MATERIAL[1]	RATE OF APPLICATION		MAXIMUM pH REACHED[2]	RESIDUAL pH AND CALCIUM	
				Material	Approximate $CaCO_3$ equivalent		pH	Exchangeable Ca
		years		*multiples of 1000 lb/acre*	*multiples of 1000 lb/acre*			*me/100 g*
Makawao silty clay loam	Haleakala Branch Experiment Station Lime Experiment	12	Reject Lime (100% $CaCO_3$ equivalent)	0	0	4.6	4.6	2.5
				4	4	5.2	4.9	4.1
				8	8	5.8	5.1	5.9
				12	12	6.2	5.2	8.0
Pauwela silty clay	Camp Maui, Grazing Trail	7	Dune Sand (65% $CaCO_3$ equivalent)	0	0	5.0	4.9	0.5
				2	1.3	5.6	5.4	1.2
				4	2.6	5.5	5.0	0.8
				6	3.9	5.9	5.2	1.2
				8	5.2	6.2	5.7	2.4
Uaoa silty clay loam	Halehaku Lime-Fertilizer Experiment	13	Reject Lime (100% $CaCO_3$ equivalent)	0	0	4.7	4.7	0.7
				1	1	4.8	4.9	0.9
				2	2	5.0	4.9	1.5
				4	4	5.4	4.9	1.9
				8	8	5.9	5.2	3.8
"	"	"	Coral Sand (95% $CaCO_3$ equivalent)	0	0	4.9	4.9	0.8
				1	0.95	5.0	4.9	0.9
				2	1.90	5.2	5.0	1.4
				4	3.80	5.5	5.0	2.0
				8	7.60	5.9	5.1	3.5

[1]Neutralizing values (percent $CaCO_3$) are estimated, with the exception of the value for dune sand reported by Younge *et al.* (1964).
[2]Maximum pH values reached for each level of lime applied are estimated from neutralization curves for the Makawao and Uaoa soils. Data for the Pauwela soil, taken from Younge *et al.* (1964), give the measured pH 1 year after lime application.

$Ca(OH)_2$ on all soils. Neutralization curves obtained with $Ca(OH)_2$ should result in the best estimate of lime requirement since the liming materials have calcium as the principal cation constituent.

Residual pH and Calcium on Limed Soils

Descriptive information pertaining to the three liming experiments from which soil was sampled is given in table 3 along with measured residual pH and exchangeable calcium data.[7] Residual calcium reflects the treatment differentials to a greater extent than pH on the Makawao and Uaoa soils. This can be seen clearly in figure 7 in which pH is related to exchangeable calcium for each experiment. Data points for the two different liming materials on the Uaoa soil are approximately on the same curve. The average slope of a straight line plotted through the Uaoa data would be nearly the same as that of the Makawao soil, indicating a consistent relationship between pH and exchangeable calcium for these two soils. Such a result might be expected in view of the high correlation between calcium saturation and pH of unlimed soils obtained by Kanehiro and Chang (1956). The reason for the relatively steep slope of the Pauwela curve is not apparent.

The relationship of residual exchangeable calcium to the calcium applied by liming is shown in figure 8. Below each data point on the residual curve is given the percent of the applied calcium which is still in the soil. Thus for the Makawao soil 39 percent of the calcium applied at the 4-me rate was accounted for as exchangeable calcium 12 years after liming. The change in residual calcium percentage with increasing rate of application is of particular interest. The low residual percentages at low application rates for the Pauwela and Uaoa soils are probably the result of crop uptake of calcium, since both soils have very low exchangeable calcium levels on the unlimed plots. The residual calcium percentage increases slightly with application rate on the Makawao soil and remains relatively constant for the Uaoa soil. The highest application rate on each soil corresponds to about half the exchange capacity (see table 2); thus a large percentage of the applied calcium could have become exchangeable. It is possible that the proportion of the applied calcium which became exchangeable increased with increasing application rate if the exchange capacity increased with increasing pH, as has been observed by Pratt (1961) and others. Mikami and Kimura (1964), however, have recently shown that for some Hawaiian soils the measured cation exchange capacity was reduced rather than

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[7]The pH and calcium data for the plot receiving 2000 pounds of liming material on the Pauwela soil are obviously not in accord with data for other plots on this soil. The plot from which the soil sample was taken is located in an area to which coral had apparently been applied prior to the establishment of the experiment. Data given by Younge *et al.* (1964) show the inconsistent pH value for this area.

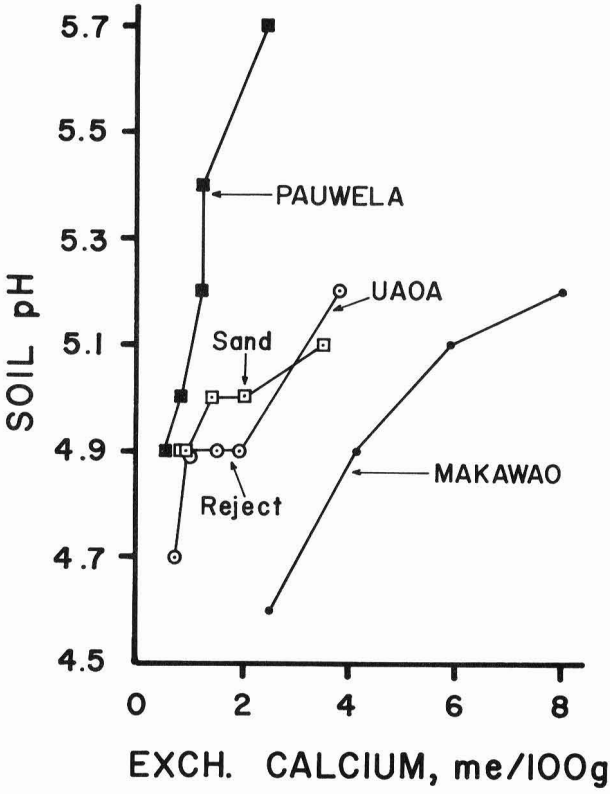

FIGURE 7. Soil pH in relation to residual exchangeable calcium several years after liming three latosolic soils.

increased by liming. Thus further interpretation of results in figure 8 awaits a better understanding of exchange reactions in Hawaiian soils.

Indications of the relative value of coral beach sand and reject lime as liming materials are given by the residual calcium curves for the Uaoa soil in figure 8 and by the residual pH data in table 3. Apparently, both materials ultimately reacted with the soil to about the same extent. There were no residual carbonates on any of the three soils, even at the highest lime rates.

Exchangeable magnesium contents corresponding to the various liming rates showed a trend of increasing magnesium content with increasing

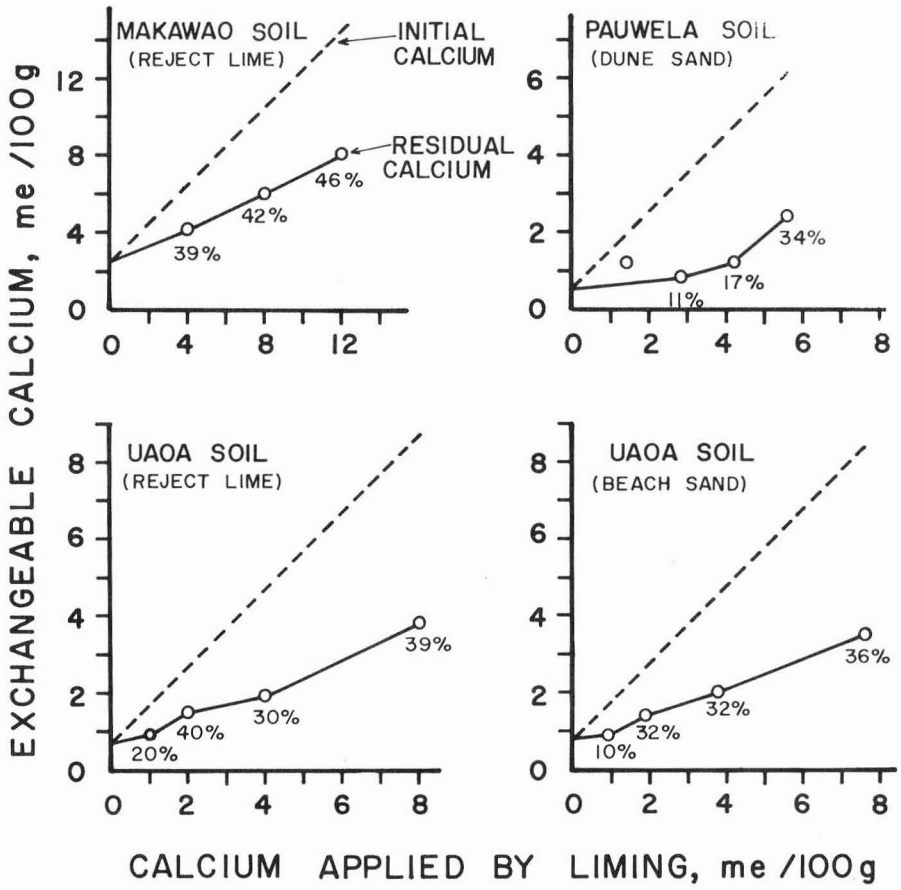

FIGURE 8. Residual exchangeable calcium in relation to the rate of applied lime on three latosolic soils. Figures below the data points give the percentage of the initial calcium (exchangeable plus applied) which is residual in the soil after several years (table 3).

liming rate. This was especially true on the Makawao and Pauwela soils, for which the magnesium contents at the highest lime rates were 0.9 and 0.8 me per 100 g, respectively, while the average magnesium contents for the other lime rates were 0.5 and 0.4 me per 100 g, respectively. This effect could be due to the magnesium present in the liming material (table 1).

DISCUSSION

Relative Value of Liming Materials

The neutralizing values and particle size distributions of the reject lime and coral sand samples studied were not greatly different. Thus the relative value of these materials is determined largely by cost, ease of handling, and reaction rate. The bulk density of reject lime is about half that of coral sand, so that hauling trucks and lime spreaders must have twice the volume capacity to haul or spread the same weight of reject lime as would be required for coral sand. However, reject lime can often be loaded in bulk from a bin at the lime kiln, eliminating the need for expensive tractor or hand loading. While the high percentage of calcium hydroxide in reject lime contributes to a greater reaction rate of large particles, it also makes the material caustic and therefore difficult to handle.

Reject lime is presently the cheapest and most reactive liming material available in the Islands, but the source is limited to about 1000 tons per year. This amount might be sufficient with the present usage (Younge and Plucknett, 1964*a*), but as the need for lime increases, coral sand and crushed coral will probably be the principal forms of liming materials used. Moberly and Chamberlain (1964) calculated the volume of sand (mostly calcareous) on the beaches of the Hawaiian Islands to be about 40 million cubic yards, with an even greater reservoir of sand below mean sea level. In addition, they estimated an average annual production of 1000 to 5000 cubic yards of sand per mile of coast from biological sources for well-developed reef areas. Thus, an adequate source of good liming material for the future is assured.

Calculated Activity of Liming Materials Based on Particle Size

Liming materials applied on an equivalent surface area basis were expected to give a predictable increase in soil pH for short reaction periods. The laboratory study showed that reasonably good estimates of pH response were obtained with coral sand for the 1-month reaction period, while reject lime was much more reactive than was predicted by surface area calculations. In the field the pH response predicted by surface area calculations was reasonably accurate for both coral sand and reject lime at 1 month, but far below the measured pH increase at 6 months.

Although estimation of lime reaction based on a reduction of particle diameter appears, in the literature, to be a more appropriate procedure for predicting ultimate pH response than surface area calculations, this method is also of limited value. The assumption of equal reduction in diameter for all sizes is invalid since large particles having a reduction in diameter equal to that of small particles will have neutralized a much larger volume of soil. Since particle dissolution is largely dependent on the acidity of soil and solution surrounding the particle, the amount of each

particle dissolved at a given time will determine the extent of further reaction.

In the present study, the volume per particle of coral sand reacting with the soil at the 30-me rate was calculated to be 0.021, 0.084, and 0.200 mm^3 for particles with mean diameters of 0.375, 0.750, and 1.30 mm, respectively. Corresponding particle diameter reductions were 0.16, 0.11, and 0.08 mm. Although the reduction in diameter of the 1.30-mm particle was only half that of the 0.375-mm particle, the volume per particle dissolved was about 10 times greater for the large particle than for the small. This result indicates that for small particle diameters, particle dissolution is restricted by the neutralizing effect of adjacent particles, while for large diameters at the same rate of application, the distance between particles minimizes the neutralizing effect of adjacent particles. The efficiency of liming materials with a high proportion of large particles should, therefore, be greater on highly buffered soils, which have a large capacity for reaction with lime, than on poorly buffered soils. The soil buffering capacity should have less effect on lime efficiency as the mean particle diameter decreases.

Liming Recommendations

The first step in the development of a liming recommendation is the accurate determination of the soil's buffering capacity for applied lime. Neutralization of soil with increments of a base in the laboratory reveals differences in buffering capacity and provides an estimate of lime requirement. The difference between the lime-requirement estimate obtained by laboratory titration and the field-measured requirement determines the appropriate "liming factor."

The laboratory estimate of lime requirement depends to some extent upon the nature of the exchanging cation used to neutralize the soil, as shown in figure 6. The difference between the NaOH and $Ca(OH)_2$ curves is probably due to the differential adsorption of Na^+ and Ca^{++} on the exchange complex. Although the relative replacing power of the various cations varies with both the exchange material and the exchanging cations, the divalent calcium ion is generally more strongly adsorbed than sodium, a highly hydrated univalent cation (Wiklander, 1955). In the present study, a comparison of laboratory neutralization curves with field pH response to liming allowed an evaluation of $Ca(OH)_2$ and NaOH as titrating bases and the calculation of appropriate liming factors. Data in figure 2 (calcium hydroxide curves) show that field pH response was accurately estimated by the reaction of $Ca(OH)_2$ with the soil in the laboratory. An application of 5 me $Ca(OH)_2$ per 100 g soil increased the pH about 0.8 in both the laboratory and field. However, titration curves obtained by adding dilute solutions of bases to soil (1:10 soil:solution mix) overestimated field pH response. If the neutralization curves for the Makawao soil in figure 6 are extrapolated to pH 4.5, the quantity of base required to increase

the pH 0.8 unit is found to be 4 me for $Ca(OH)_2$ and 2 me for NaOH. Thus for this soil the liming factor would be 1.25 using the $Ca(OH)_2$ curve and 2.5 using the NaOH curve.

If the liming material used in the field is composed wholly of fine particles, the "liming factors" determined for neutralization curves should result in good estimates of pH response in the field. However, if the liming material contains a large percentage of coarse particles, as did the coral sand and reject lime used in this study, another correction must be made for the efficiency of the material. The efficiency ratios in figure 5 (10-me rate) indicate correction factors of 1.3 for reject lime and 1.5 for coral sand. The fact that these values are as large or larger than the liming factor determined above for the calcium hydroxide neutralization curve emphasizes the importance of evaluating the liming material in the development of a lime recommendation. Lime efficiency ratios determined in the laboratory under optimum moisture conditions may overestimate the effectiveness of lime applied in the field where low moisture conditions may hinder the rate of lime reaction. Data in figure 2 indicate that limited soil moisture may have retarded the reaction rate of both coral sand and reject lime in the field, but the ultimate pH response to coral was the same in the laboratory and field. The reaction rate of reject lime is probably affected more by soil moisture than that of coral sand due to the rapid solution of reject particles in water, as discussed previously.

Another factor affecting the accuracy of liming recommendations is the soil-weight conversion factor. Liming recommendations based on a laboratory determination of the soil buffering capacity generally assume a soil-weight conversion factor to convert the laboratory unit, me per 100 g, to the field application rate expressed in pounds of liming material per acre. If the field soil layer to which lime is applied weighs 2 million pounds, 1 me per 100 g is equivalent to 1000 pounds of calcium carbonate per acre. This conversion is convenient and widely used, often without regard for the soil bulk density or the soil depth to which lime is being applied. Such considerations are important in Hawaii, where the bulk density of surface soils may vary from 0.5 g per cm^3 (or less on ash-derived Hydrol Humic Latosols) to 1.4 (or more on some soils). Depth of lime incorporation may vary from about 6 inches on soils cropped with vegetables or flowers to about 15 inches on soils planted to sugarcane or pineapple.

The calculated weights of an acre-plow-layer as affected by variations in soil depth and bulk density are shown in table 4. It is apparent from the table that considerable error could be made by assuming a standard laboratory-to-field conversion factor. Application of lime to a depth of 7 inches on a soil with a bulk density of 0.5 g per cm^3 and at a rate based on a field soil weight of 2 million pounds per acre would result in overliming by a factor of $(2)/(0.79)$, or 2.53. On the other hand, a recommendation

TABLE 4. Relationship between soil bulk density and weight of an acre-soil-surface layer of varying thickness

SOIL BULK DENSITY	ACRE WEIGHT (IN MILLIONS OF POUNDS) OF SOIL SURFACE LAYER OF DESIGNATED DEPTH*					
	6 inches	7 inches	8 inches	10 inches	12 inches	14 inches
g/cm^3						
0.5	0.68	0.79	0.91	1.13	1.36	1.58
0.6	0.82	0.95	1.09	1.36	1.63	1.90
0.7	0.95	1.11	1.27	1.59	1.90	2.22
0.8	1.09	1.27	1.45	1.81	2.17	2.54
0.9	1.22	1.43	1.63	2.04	2.45	2.85
1.0	1.36	1.59	1.81	2.27	2.72	3.17
1.1	1.50	1.74	1.99	2.49	2.99	3.49
1.2	1.63	1.90	2.17	2.72	3.26	3.80
1.3	1.77	2.06	2.36	2.94	3.53	4.12
1.4	1.90	2.22	2.54	3.17	3.81	4.44
1.5	2.04	2.38	2.72	3.40	4.08	4.76

*The horizontal line in each column indicates the approximate bulk density and soil depth corresponding to an acre-plow-layer weighing 2 million pounds.

based on the standard conversion would underestimate the liming rate by a factor of 2.06 on a soil having a bulk density of 1.3 g per cm^3 and being limed to a depth of 14 inches.

SUMMARY AND CONCLUSIONS

Liming of soils in Hawaii has become increasingly important as soil pH and calcium levels decrease with intense cropping and as more high-rainfall areas are developed for improved pastures and other crops. Accurate liming recommendations require an evaluation of the properties of both the soil and the liming material.

The efficiencies of calcareous beach sand and reject lime, as influenced by the chemical and physical properties of each liming material, were evaluated in the laboratory and field. Both materials are characterized by a high neutralizing value, sufficient fineness, and a desirable magnesium content. "Coral" beach sand is derived from the skeletal remains of a number of marine organisms which differ in mineralogical and chemical composition. Beach sand contains both calcite and aragonite while reject lime contains calcite only. The calcium hydroxide content of reject lime renders it more water-soluble than coral sand and thus more readily active. Accordingly, the reductions in efficiency due to either increased particle size or increased rate of application are much greater for coral sand than for reject lime.

Estimates of field liming rates based on laboratory neutralization curves must take into account (1) the discrepancy between laboratory and field pH response to applications of readily active lime and (2) the efficiency of the liming material applied in the field. On the Makawao soil a $Ca(OH)_2$ neutralization curve overestimated field pH response by a factor of 1.25. Measured efficiency ratios for the unsegregated coral sand and reject lime used in this study were 0.65 and 0.75, respectively, for a 3-month reaction period. Thus, if a $Ca(OH)_2$ neutralization curve indicated the need for 5 me $Ca(OH)_2$ for the desired increase in pH, the amount of coral sand to apply in the field would be (5)(1.25)(1/0.65), or about 9.6 me per 100 g soil. The "liming factor" in this case would be (1.25)(1/0.65), or 1.92. The efficiency of liming material may be expected to vary somewhat for different soils and for different soil moisture levels and tillage practices. It should be kept in mind that the efficiency ratios used here are based upon a 3-month reaction period; longer reaction times would have yielded higher efficiency ratios. Also, materials derived from other calcareous deposits in Hawaii might have given somewhat different results.

The usefulness of calculated lime activity based on the specific surface of particles and on the reduction of particle diameter with particle dissolution was studied with both coral sand and reject lime. Specific surface calculations appear to provide reasonably good estimates of short-term pH response in the field. Since it is often desirable to know the pH level a month or less after liming, such estimates of lime activity could be of practical importance. At the optimum moisture level maintained in the laboratory study, reject lime was much more reactive than surface area calculations predicted. Measured lime particle reaction rates showed that both the quantity of lime applied and the particle diameter influenced the extent of the reduction in particle diameter upon particle dissolution. Thus the usefulness of predictions based on the hypothesis of equal reduction in particle diameter appears limited. The calculations did show the effect of spatial distribution of lime particles on particle dissolution. At a given rate of application, the large particles, being widely spaced, reacted to a much greater extent than the closely spaced small particles for which dissolution was limited by the neutralizing effect of adjacent particles. This effect was much more evident for the slowly soluble coral sand than for reject lime.

The residual effects of liming were studied by analysis of soil samples from three old liming experiments on Maui. Residual pH and calcium values measured on the Uaoa soil 13 years after liming with coral sand and reject lime showed that the two materials were equally effective. Exchangeable calcium reflected treatment differentials to a greater extent than did pH, especially on the soils limed 12 and 13 years previous to the analysis. As much as 46 percent of the applied calcium was still in the Makawao soil 12 years after liming.

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APPENDIX

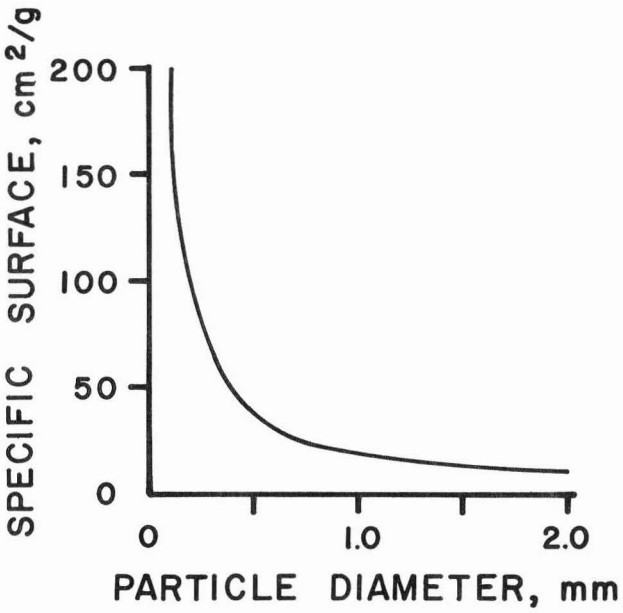

FIGURE A-1. Relationship of specific surface to particle diameter for spherical particles with a density of 2.9 g/cm³.

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